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Self-Assembly of Ordered Microporous Materials  
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By

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## **Self-Assembly of Ordered Microporous Materials from Rod-Coil Block Copolymers**

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### **Abstract**

Rod-coil diblock copolymers in a selective solvent for the coil-like polymer self-organize into hollow spherical micelles having diameters of a few micrometers. Long-range, close-packed, self-ordering of the micelles produced highly iridescent periodic microporous materials. Solution cast micellar films consisted of multilayers of hexagonally ordered arrays of spherical holes whose diameter, periodicity, and wall thickness depended on copolymer molecular weight and composition. Addition of fullerenes into the copolymer solutions also regulated the microstructure and optical properties of the microporous films. These results demonstrate the potential of hierarchical self-assembly of macromolecular components for engineering complex two- and three-dimensional periodic and functional mesostructures.

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Ordered mesoporous solids with nanoscale pore sizes are of interest in areas such as catalysis, sensors, size- and shape-selective separation media, adsorbents, and scaffolds for composite materials synthesis (1-2). Those with pore sizes on the order of 50 nm to 10  $\mu$ m are also of interest for applications in photonics, optoelectronics, light-weight structural materials, and thermal insulation (2-5). Most current general methods for preparing diverse porous materials use self-organized surfactants, block copolymers, or colloidal particles as templates in conjunction with sol-gel techniques (1-3). In these methods, the organic templates are eventually removed by thermal decomposition or solvent extraction to achieve the porous solid. Recently reported hollow spherical micelles of rod-coil diblock copolymers (6) represent a novel class of colloidal particles (7). Their self-organization into long-range crystalline order could open the way to novel colloidal crystals (8-9), unusual microgels, and direct self-assembly of ordered microporous materials.

Polymer latex and silica spheres are known to form colloidal crystals (8-9), but long-range ordering of suspensions of block copolymer micelles into body-centered cubic (bcc) and face-centered cubic (fcc) lattices was observed and elucidated more recently (10). Micelles of coil-coil block copolymers in a selective solvent for one of the blocks are spheres consisting of a dense core of the insoluble block and a diffuse corona of the solvated block (10-12). Copolymer architecture and solution chemistry have been used to vary their diameter between about 10 to 80 nm and the corona thickness relative to the core radius (10-12). Micellar crystallization into either an fcc or a bcc lattice is determined by the length scale and steepness of repulsive interactions that can be controlled by the ratio of the coronal layer thickness to the core radius (10). However, the implications of the unusual micellar structures of rod-coil block copolymers (6, 13) for regulating these repulsive interactions, micellar crystallization, and crystal lattice selection are yet to be investigated.

We report the self-organization of hollow spherical micelles from a rod-coil diblock copolymer system in a selective solvent for the flexible-coil block and their long-range, close-packed, self-ordering into iridescent, ordered microporous solids. This hierarchical self-assembly approach to microporous solids represents a non-template strategy (Fig. 1). The micellar structure, consisting of a hollow core, a rodlike inner shell, and a flexible-coil outer corona, has a diffuse corona characteristic of coil-coil block copolymer micelles (10, 12). Steric repulsion driven self-ordering and crystallization of coil-coil diblock micelles and their demonstrated control through the corona block length (10) are thus also viable options here. The rod-coil diblock copolymer system we investigated is poly(phenylquinoline)-*block*-polystyrene (PPQ<sub>m</sub>PS<sub>n</sub>, where m and n are the number of repeat units of the respective blocks) in carbon disulfide (CS<sub>2</sub>) which is a selective solvent for PS block. The specific diblock compositions we studied are PPQ<sub>10</sub>PS<sub>300</sub>, PPQ<sub>10</sub>PS<sub>1000</sub>, and PPQ<sub>50</sub>PS<sub>2000</sub> which are either identical to those we previously reported (6, 13) or similarly made. The basic synthetic chemistry is that associated with the rigid, rodlike conjugated PPQ homopolymer (14) which is highly fluorescent and has nonlinear optical properties (15).

We investigated solutions (0.005 to 1.0 wt % diblock) in CS<sub>2</sub> and monolayer and multilayer films cast from them at room temperature (25°C). Direct optical, fluorescence, and scanning electron microscopy observations of discrete micellar aggregates and their higher order assembly into large-scale periodic microstructures were made. The possible effects of both the local structure of the micellar building block and the large-scale periodic microstructure on the spontaneous emission of the PPQ chromophores of the diblocks were probed by previously described steady-state and time-resolved photoluminescence techniques (16).

Theoretical studies of the possible equilibrium structures of micelles of rod-coil block copolymers in a selective solvent for the coil-like block have been reported (17). Because of the

difficulty of efficient space-filling packing of rodlike blocks into a spherical or a cylindrical core, various alternative space-filling core-corona models, such as disklike cylindrical micelles and monolayer and bilayer "hockey puck" micelles, have been proposed (17). However, experimental data have heretofore been unavailable to test these models (18). Our experimental results show that rod-coil diblock chains solve the steric problem associated with packing rodlike blocks radially into a sphere in a surprising way not anticipated by theory: A hollow sphere. Fluorescence photomicrographs of micelles formed by PPQ<sub>10</sub>PS<sub>300</sub> in CS<sub>2</sub> provide evidence of hollow spheres (Fig. 2, A and B). The shape of the discrete micellar aggregates look somewhat like red blood cells because of distortion and partial collapse of the hollow spheres due to drying. Additional microscopic observations under bright field and crossed polarizers confirmed that the micelles formed by all three copolymer samples had approximate diameters of 3 to 5  $\mu\text{m}$ . Polarized optical microscopy indicated that the micelles were highly ordered. This ordering originates from orientationally ordered radial packing of the rigid, rodlike blocks; micellar aggregates of coil-coil block copolymers lack such order (11-12). The hollow spherical structure of these rod-coil diblock micelles in CS<sub>2</sub> is, however, different from that formed by the same copolymers in trifluoroacetic acid/dichloromethane (a selective solvent for the rodlike blocks) (6,13) in that here the solvated coillike blocks are on the convex side. A profound consequence of the stiffness asymmetry of a rod-coil diblock copolymer is thus that the same macromolecule in two different selective solvents can self-organize into two qualitatively different colloidal particles: Hollow hard spheres and hollow soft spheres.

Self-ordering of these hollow soft spheres into two-(2D) and three-dimensional (3D) periodic structures was studied by optical and electron microscopy of micellar films cast from diblock solutions of varying initial concentrations in ways similar to prior studies of colloidal crystallization of polymer latex spheres (8-9). Only discrete, non-aggregated, micelles were

obtained from very dilute solutions between 0.005 to 0.01 wt % (Fig. 2, A and B). However, even at 0.01 wt %, the particle number density is sufficiently high for the onset of 2D micellar ordering to be visible in regions of a monolayer film (Fig. 2B, arrows). Micellar films cast from 0.5 wt % had a controllable thickness of about 4.5 to 35  $\mu\text{m}$  and consisted of stacks of one to eight layers of hexagonally close-packed (hcp) 2D lattices of spherical air holes in a polymeric matrix. An example is the  $\sim 27\text{-}\mu\text{m}$  thick micellar film of PPQ<sub>10</sub>PS<sub>300</sub> which reveals a 2D hcp structure when viewed from the top (Fig. 2C) and was visually highly iridescent at various reflection angles akin to a credit card hologram. The air holes revealed by carefully peeling off part of the top layer with an adhesive tape largely reflect the original hollow spherical micelles. The moderate mechanical properties of these self-ordered micellar films suggests that significant interdigitation of the polystyrene coronal chains occurs between the micellar building blocks of the microporous solid.

Defect-free microstructure of the periodic microporous films of all three block copolymers covered areas as large as 1  $\text{cm}^2$  and varied with composition and molecular weight. From the polarized optical and scanning electron (SEM) micrographs of micellar films of PPQ<sub>50</sub>PS<sub>2000</sub> (Fig. 3 A to C), 2D hcp lattice of spherical air holes having a diameter ( $D$ ) of  $3.4 \pm 0.2 \mu\text{m}$  and a center-to-center hole periodicity ( $p$ ) of  $4.4 \pm 0.2 \mu\text{m}$  were observed from the top layer. The  $\sim 31\text{-}\mu\text{m}$  film consisted of seven layers of air hole lattices of which the top layer is clearly open (Fig. 3, B and C). The progressive decreases of the hole diameter and periodicity of the microstructure with the PS block length were approximately linear (Fig. 3D), decreasing to  $2.6 \pm 0.2$  and  $2.8 \pm 0.2 \mu\text{m}$ , respectively, for micellar films of PPQ<sub>10</sub>PS<sub>300</sub>. The minimum wall thickness  $h$  ( $= p-D$ ), which was in the range of 0.2 to 1.0  $\mu\text{m}$  for the three copolymer compositions, also varied linearly with the PS coronal chain length. Evidence of the 3D order of

these multilayer films include their colorful iridescence (2, 8, 9) and observation of ordered arrays of the air holes when multilayer films were viewed from the side or by sequential removal of layers from the top(19).

Addition of small amounts ( $< 20$  mg/g diblock) of fullerene ( $C_{70}$  or  $C_{60}$ ) into the solutions in  $CS_2$  significantly modified the microstructural parameters of the ordered microporous films (Fig. 4). Although these fullerene-containing micellar films had superior iridescence colors compared to similar microporous films without fullerene, they were more brittle with visible cracks. The hole diameter and periodicity decreased with amount of fullerene loading, up to 29 and 25% reductions, respectively, at 10 mg  $C_{70}$  /g PPQ<sub>10</sub>PS<sub>300</sub> (Fig. 4B). The wall thickness increased slightly with fullerene loading. Similar effects of fullerene  $C_{70}$  or  $C_{60}$  on self-organized microporous films of PPQ<sub>10</sub>PS<sub>1000</sub> and PPQ<sub>50</sub>PS<sub>2000</sub> were observed. Self-assembly of microporous films was no longer observed in any of the three diblock copolymers at high fullerene loading ( $> 20$  mg/g). These results suggest that the fullerene is incorporated within the PS corona of the micellar building blocks as expected from their mutual compatibility (6). These findings also suggest a simple way of controlling the functional properties of the microporous materials independently of copolymer architecture and composition.

Because of their spatially periodic variation of refractive index, these self-organized ordered microporous materials with or without fullerenes are promising, easy to produce, photonic band gap structures (2, 4). These periodic dielectric composites of air holes (refractive index  $n_o = 1$ ) and diblock walls ( $n_o = 1.6$  for PS, 1.8 for PPQ) have a high refractive index contrast. The higher index contrast in fullerene-containing micellar films,  $C_{70}$  ( $n_o = 1.94$ ) and  $C_{60}$  ( $n_o = 2.00$ -2.12) (20), can explain their superior optical properties. However, the present hole diameters and periodicities are comparable to infrared (IR) wavelengths. Reductions in  $D$  and  $p$



to sizes comparable to visible wavelengths are desirable for some photonic and optoelectronic applications (4).

Significant modification of the spontaneous emission of the PPQ blocks in the self-assembled, periodic microporous films, compared to the isolated chromophores dispersed in a matrix of poly(ethylene oxide) (PEO), was observed by photoluminescence emission (PL) and excitation (PLE) spectroscopies (Fig. 5). Isolated PPQ chromophores of PPQ<sub>10</sub>PS<sub>300</sub> diblock have emission and excitation bands at 466 and 393 nm, respectively. In contrast, the micellar films of PPQ<sub>10</sub>PS<sub>300</sub> cast from a 0.5 wt % solution have blue-shifted PL and PLE spectra with peaks at 437 and 388 nm, respectively, (Fig. 5A), and absorption band observed in the PLE is more narrow. Time-resolved PL decay dynamics of the fluorescent PPQ blocks as isolated chains in PEO revealed two lifetimes [1.1 ns (30%) and 4.7 ns (70%)] versus one lifetime (0.93ns) (Fig. 5B) in the micellar films. This represents a large reduction in the excited state lifetime of PPQ chromophores in the microporous micellar films. Because the emission band is far removed from photonic band gaps of these microporous films, which are expected to be in the IR region, we rule out the large-scale periodic microstructure as the origin of the observed modification of photophysical properties. The decrease in lifetime is also the opposite of the predicted effect of a photonic crystal on spontaneous emission (4). H-aggregation (21) of the PPQ blocks and hence the local structure of the micellar building blocks best explain the observed photophysical properties. H-aggregation of the rigid rodlike blocks implies that they are orientationally aligned close to the radial direction in the spherical micellar assemblies (Fig. 1). Such an H-aggregation of conjugated molecules can lead to novel cooperative optical and nonlinear optical properties (21).

Because the size, mesostructure, and properties of micellar building blocks can be tailored through copolymer architecture and composition as well as the solution chemistry (10-

13), we suggest that this hierarchical self-assembly approach is quite general for preparing periodic mesoporous polymeric materials. Besides photonic band gap materials and their associated applications (4), the ordered micellar films and their self-assembly process may have uses as models in tissue engineering and biomaterials (22), fabrication of molecular electronic devices (23), optically tunable and responsive coatings, and processing of "soft" colloidal materials. By combining different micellar building blocks and colloidal particles such as dendrimers or polymer lattices, self-assembly of very unusual periodic mesoscopic structures with tailorable functions may be possible.

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  19. Distinction between ABCABC- or ABABAB-type stacking of layers and hence whether the 3D lattice was fcc or hcp could not be established.
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  24. This research was supported by the Office of Naval Research and in part by the National Science Foundation (CTS-9311741, CHE-9120001) and an Elon Huntington Hooker Fellowship to X. L. C.

## Figure Captions

- Fig. 1.** Molecular structure of the rod-coil diblock copolymer  $PPQ_mPS_n$  and schematic illustration of its hierarchical self-assembly into ordered microporous materials.
- Fig. 2.** Fluorescence photomicrographs of solution cast micellar films of  $PPQ_{10}PS_{300}$  obtained by ambient air drying of different diblock solution concentrations in  $CS_2$ : (A) 0.005 wt %; (B) 0.01 wt %; and (C) 0.5 wt %. Arrows in **B** indicate regions of self-ordering.
- Fig. 3.** (A) Polarized optical and (B and C) SEM micrographs of microporous micellar films obtained from a 0.5 wt %  $PPQ_{50}PS_{2000}$  diblock solution by solution casting on a glass slide and an aluminum substrate, respectively. The SEM samples were coated with a 10-nm gold layer. The SEM image in **B** is the top view and that in **C** is of the same sample tilted  $45^\circ$  from the beam axis to reveal 3D structure. (D) variation of hole diameter ( $D$ ), periodicity ( $p$ ) and minimum wall thickness ( $h$ ) of ordered microporous films with the number of PS repeat units in the diblocks.
- Fig. 4.** (A) Polarized optical micrograph of a microporous micellar film of  $PPQ_{10}PS_{300}$  obtained from a 0.5 wt % solution containing 5 mg  $C_{70}$  /g diblock. (B) Dependence of microstructural parameters of micellar films of the same diblock on fullerene loading.
- Fig. 5.** (A) PL emission (390-nm excitation) and PLE excitation (460-nm emission) spectra of a micellar film of  $PPQ_{10}PS_{300}$  and of the same diblock chains homogeneously dispersed (0.1 wt %) in a poly(ethylene oxide) (PEO) film. (B) PL decay dynamics of the same samples in A when excited at 360 nm and monitored at 490 nm.

Figure 1

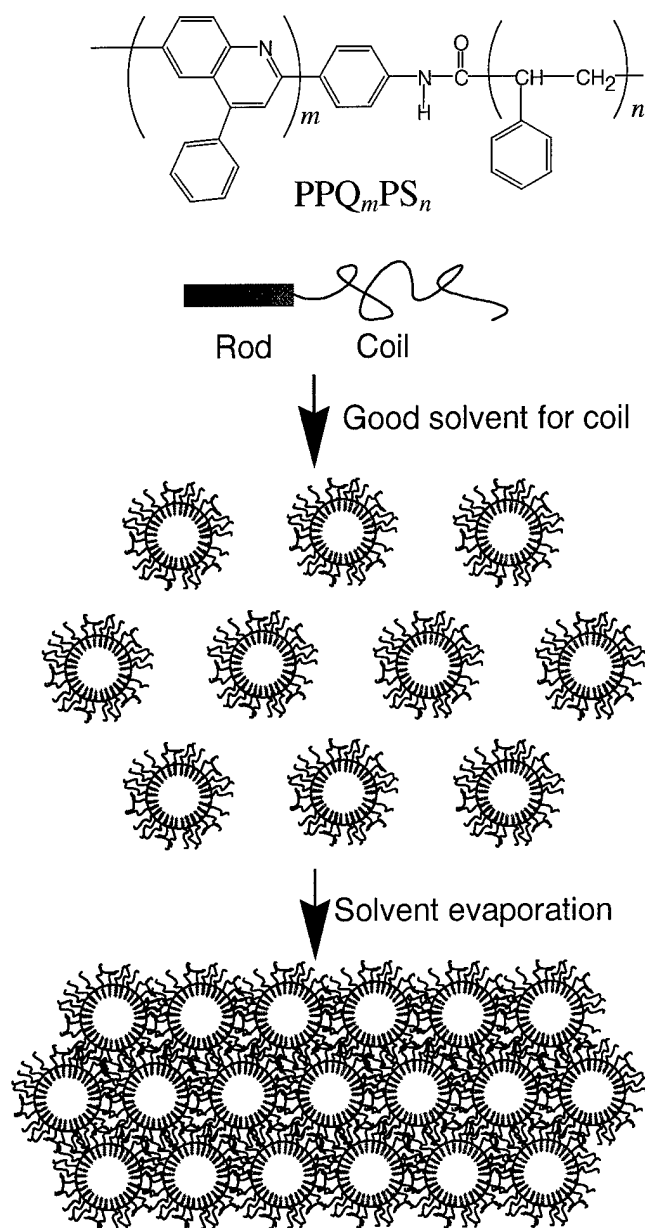


Figure 2

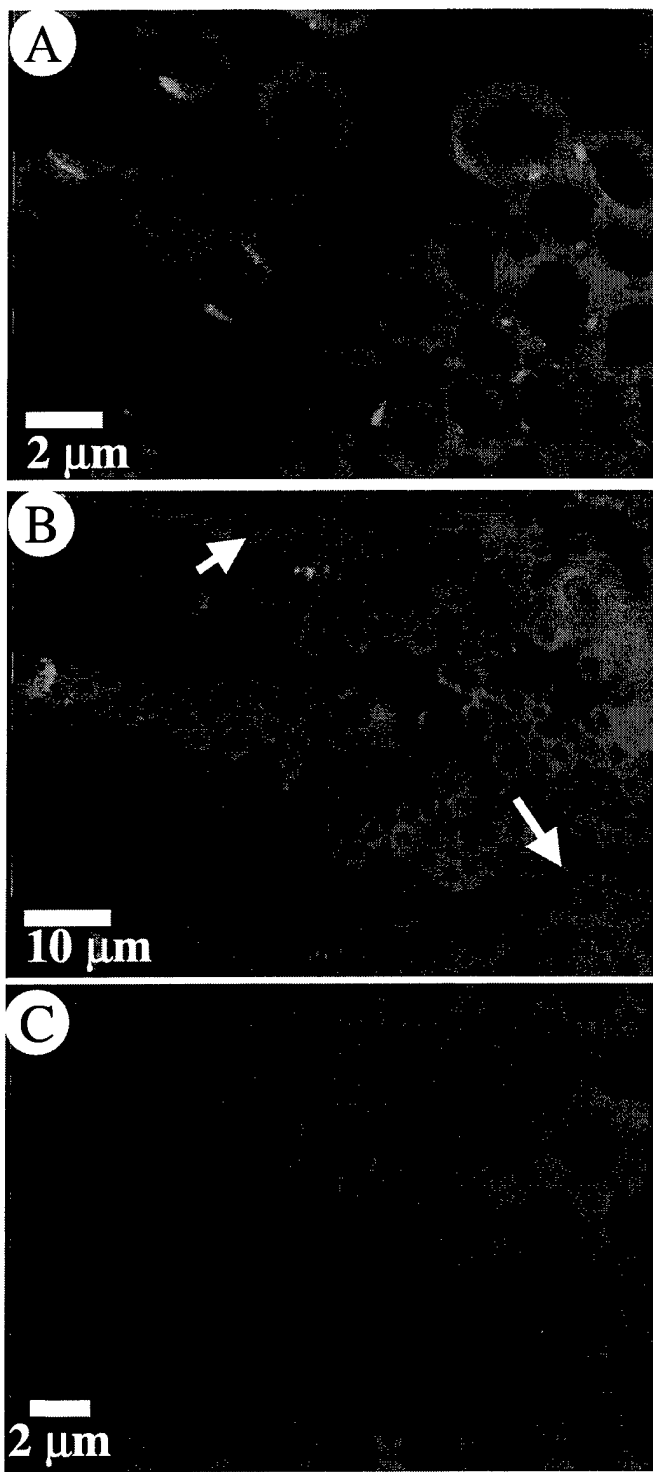




Figure 3

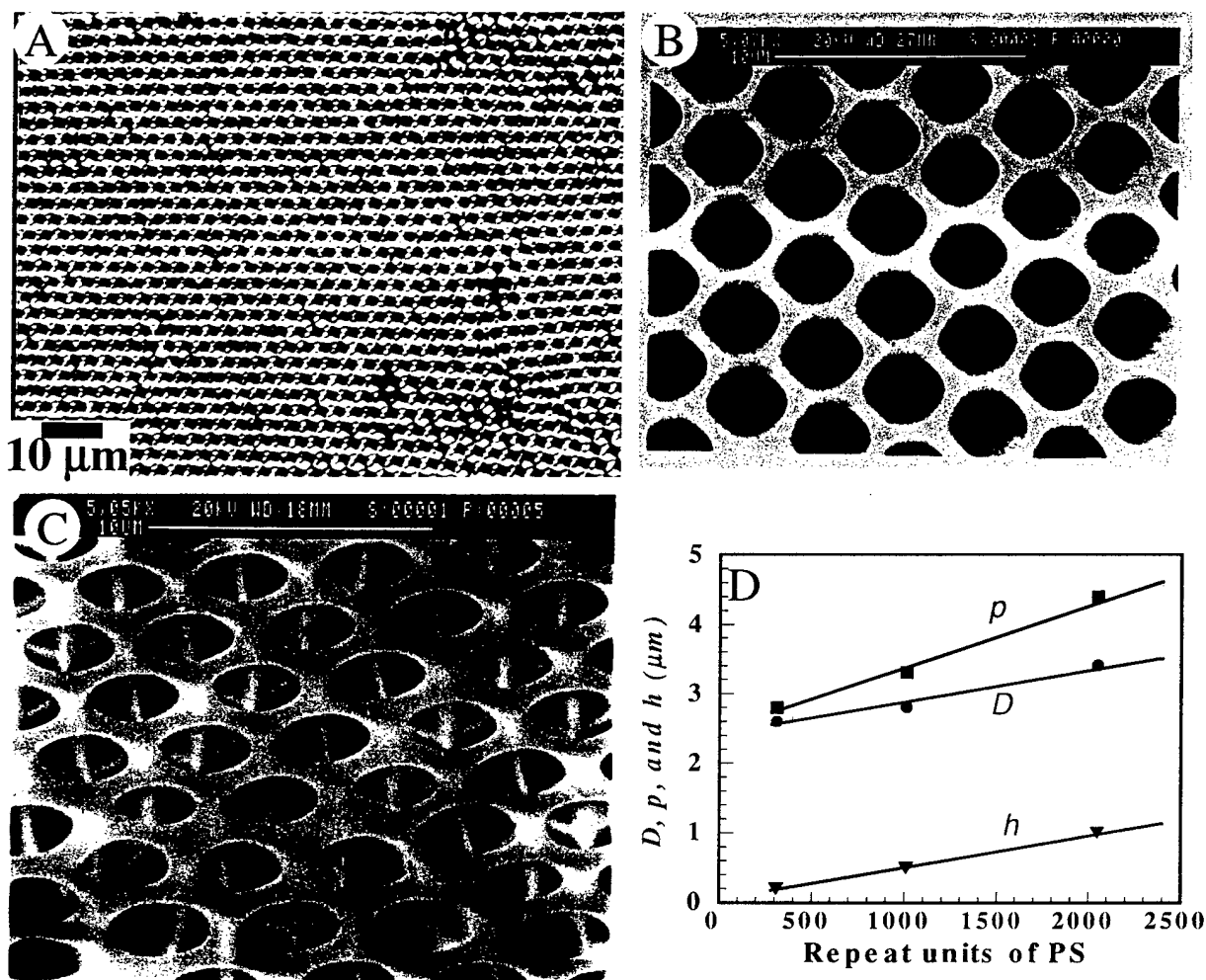


Figure 4  
Jenekhe

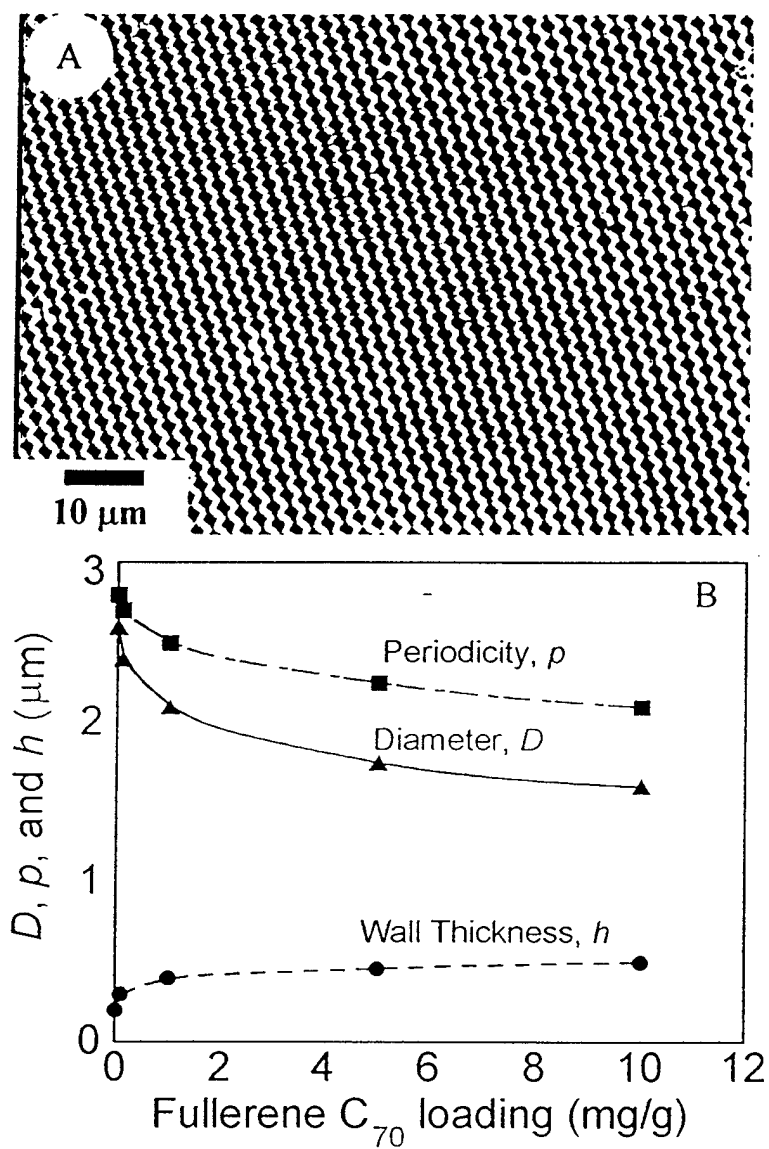


Figure 5

